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INVESTIGATION OF THE THERMOPHYSICAL PROPERTIES OF HIGH-MELTING MATERIALS WITH THE AID OF A COMPLEX OF INSTRUMENTS

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16. Abstract

The evaporation rate, vapor pressure, heats of evaporation reaction (sublimation, dissociation); enthalpy, electrical resistance, heat capacity, emissivity, and heat conductivity of various carbides, borides, sulfides, nitrides, selenides, and phosphides were investigated. A set of high temperature high vacuum devices; calorimeters (designed for operation at 400 to 1300 K and from 1200 to 2500 K), and mass spectrometers, most of which were specially developed for these studies, are described.

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The growth of various branches of new technology is intimately /135* associated with the development and search for materials with improved properties. Special attention is given here to finding high temperature, heat resistant, durable and other materials. It is possible to solve this problem by comprehensive study of different thermophysical properties of promising materials. Investigation of the evaporation properties, measurement of the melting temperature and temperature relationships of the evaporation rate (partial pressures, vapor components), enthalpy, electrical resistance, emissivity and heat conductivity permit determination of the fields of use of various materials. In addition, technologically important thermodynamic characteristics of the materials can be obtained as a result of such studies. Finally, comparison of the thermophysical characteristics with the characteristics of electron structure permits determination of the nature of the chemical bonding of compounds and is a basis for the development of theoretical prerequisites of the development of materials with preassigned properties.

In order to conduct thermophysical investigations of high-melting materials, an instrument complex was set up and methods were developed for study of evaporation characteristics and rate, vapor composition and pressure, heats of the evaporation reactions (sublimation, dissociation, disproportionation), enthalpy and heat capacity, electrical resistance, emissivity and heat conductivity over a wide temperature range and for melting temperature measurement.

The equipment complex includes a high temperature, high vacuum unit [1], high temperature, high vacuum unit with automatic vacuum

*Numbers in the margin indicate pagination in the foreign text.

balance [2], MI-1305 mass spectrometer adapted for high temperature investigations [3] and mixing calorimeters operating at 400-1300 K and 1200-2500 K [4].

The high temperature, high vacuum unit with specimen heating by direct transmission of current is intended for measurement of the temperature dependence of electrical resistance, monochromatic emissivity ε_λ (λ=0.65 μm), coefficient of heat conductivity and evaporation rate.

For determination of electrical resistance, the probe method of measurement of the voltage and current drop on an isothermal section of the specimen was used. Temperature vs. coefficient of heat conductivity was determined by a modified electrical method [1]. Determination of temperature vs. emissivity is based on comparison of the brightness temperature of the specimen surface and a hole which simulates an ideal black body. It was determined by test that a 0.9-1 mm diameter hole at least three diameters deep can be an ideal black body for the specimens used (cylinder 18-25 mm high, 6-7 mm diameter).

To make measurements by the methods specified, besides the holes which simulate a black body located in the middle part of the specimen, holes also were made at distances of 6-7 mm from the ends.

In the next stage of the studies, the melting temperature was determined from the middle hole (appearance of a liquid drop in it).

Finally, from measurements of the weight losses from a known surface of the same specimens in a specific time interval (periodic weighing, Langmuir method), the evaporation rate was determined.

The unit consists structurally of a vacuum chamber, evacuation system and control panel, on which the measuring system components, /136
control system and vacuum and power unit displays are located. The basic part of the unit is the steel vacuum chamber (Fig. 1), the

covers and walls of which are cooled by circulating water. The bottom current lead is a fixed copper platform, but the top one, also made of copper, can be moved without breaking the vacuum. The ends of both electrodes are fitted with removable tungsten inserts, and they also are water cooled.

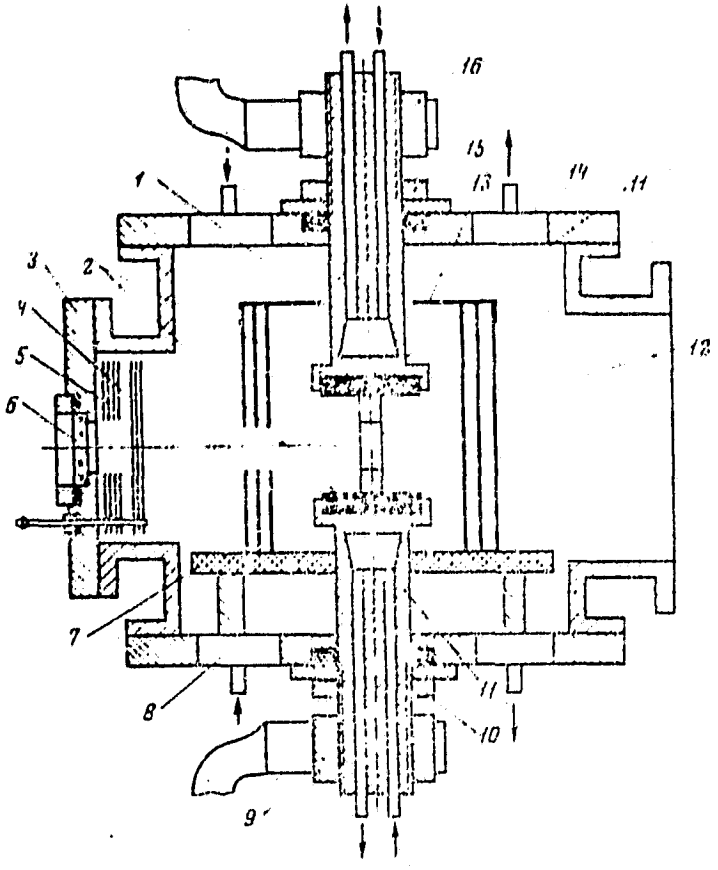

Fig. 1. Diagram of unit for investigation of thermophysical properties of high-melting materials: 1. chamber body; 2. tungsten electrodes; 3. side cover; 4. shutters; 5. nickel shields; 6. inspection window; 7. shield platform; 8. bottom cover; 9. bottom current leads; 10. lower current lead seal; 11. copper electrodes; 12. specimen; 13. nickel shields; 14. top cover; 15. top current lead seal; 16. top current lead.

A system of vacuum shutoffs and valves permits the cooled chamber to be filled with air without breaking the vacuum of the entire system.

The vacuum is obtained in the chamber (no worse than $2 \cdot 10^{-5}$ mm Hg at 2000-4000 K) by means of a VA-2-3 vacuum set and a VN-2 forevacuum pump, and preliminary evacuation of the chamber in overloads is obtained with a RVN-20 forevacuum pump. The power portion of the unit consists of a OSU-20 stepdown transformer and a RNO-10 voltage regulator. It permits temperatures on the order of 4000 K to be obtained. Temperatures are measured through an inspection window with an OMP-019 pyrometer.

Together with the basic advantage, which consists of simultaneous measurement of a number of characteristics on one specimen, the method under consideration has disadvantages associated with the possibility of study of only current conducting specimens. Besides, despite high sensitivity, this equipment permits measurement of the evaporation /137
rate with an error of at least 25% with low output and in the absence of equilibrium between the solid and vapor phases. The evaporation rates measured in this unit are of an applied nature, since they are measured under conditions which reproduce the actual conditions of utilization of high-melting compounds. Moreover, the evapo- /138
ration rate measured under equilibrium conditions is the basis for various thermodynamic calculations. To obtain the equilibrium evaporation rates, the high temperature, high vacuum unit with the automatic vacuum balance [2] is used. Measurements in it are preferably made by the Knudsen method.

This unit consists structurally of the high vacuum chamber, in which the high temperature furnace and vacuum balance are located (Fig. 2), the evacuation system and the control panel.

The high temperature furnace is mounted on the bottom water cooled flange of the high vacuum chamber, and it is a cylindrical graphite heater (inside diameter 30 mm, height 140 mm), connected to the water cooled copper electrodes, and the thermal insulation shield system. The power portion of the unit consists of an OSU-20/05 step-down transformer, to the primary circuit of which a RNO-10 voltage regulator is connected. This furnace and power unit design ensures that 2500 K is reached.

The automatic microanalytic balance is installed on a water coled flange in the top portion of the high vacuum chamber. The balance has electromagnetic control and damping and a photoelectric out of balance indicator, and it is built on the base of a VM-20M balance. The sensitivity of the modified balance is 5.10^{-5}g.

The effusion cell on a tungsten suspension is placed in the

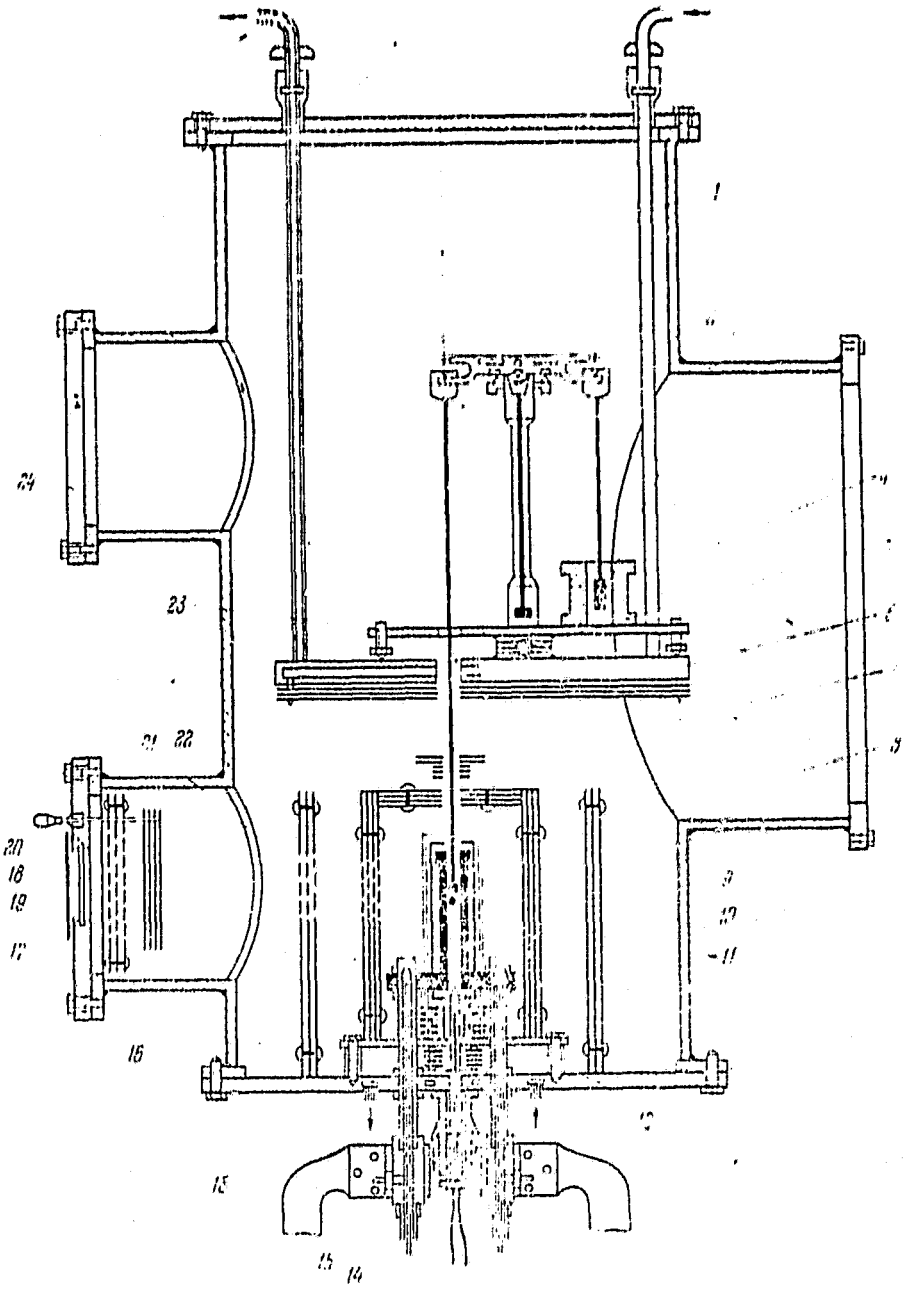

Fig. 2. Diagram of working chamber of unit for study of evaporation: 1. holder of water cooled slab; 2. VM-20 semimicroanalytic balance; 3. permanent magnet; 4. solenoid; 5. locking device; 6. water cooled slab; 7, 8. molybdenum shields; 9. heater; 10. graphite shields; 11, 20. nickel shields; 12. copper plate; 13. current leads; 14. thermocouple; 15. contact holder; 16. chamber housing; 17. flange; 18,24. inspection windows; 19. window shutter; 21. electrode; 22. effusion chamber; 23. supporting screw.

middle part of the high temperature furnace. The cell temperature is measured with an OMP-043M optical pyrometer through an inspection window, openings in the thermal insulation shields and a slit in the graphite heater from a hole which simulates a black body made in the side wall of the cell. The temperature measurement error is 0.8%.

The vacuum in the chamber (at least $5 \cdot 10^{-7}$ mm Hg during nitrogen trap operation and $5 \cdot 10^{-6}$ mm Hg without freezing of the vapors at 2000-2500 K) is obtained by means of a VA-5-4 vacuum unit and VN-1 forevacuum pump, and preliminary evacuation of the chamber under load, with a VN-2 forevacuum pump.

Measurements in the unit with the automatic vacuum balance permit determination of the equilibrium evaporation rate over a wide temperature interval and calculation of the absolute partial pressures of the vapor components. The latter values combined with chemical and X-ray analysis results on the solid phase permit determination of the thermodynamic characteristics of the reactions due to the transition of the solid phase to vapor at the average test temperatures. The vapor composition must be known however for calculation of the partial pressures of the vapor components from the measured evaporation rates.

The most widespread method of determination of the composition of high-melting material vapors is high temperature mass spectrometry [5]. A modified MI-1305 mass spectrometer was used to carry out the mass spectrometric analysis [3]. The changes incorporated in the design of the instrument (Fig. 3) consisted of installation /139
of a pyrometry window in the analyzer chamber, through which the temperature of objects can be determined pyrometrically by means of a OMP-043 micropyrometer to within 0.8% in the 1300-4000 K temperature interval. To obtain temperatures on the order of 2500 K and carry out evaporation under Knudsen conditions, vaporizers developed at the Ukrainian SSR Academy of Sciences Institute of the Physics of Materials was used [6]. In vaporization under Langmuir conditions, "combustion boat" type vaporizers similar to those in-

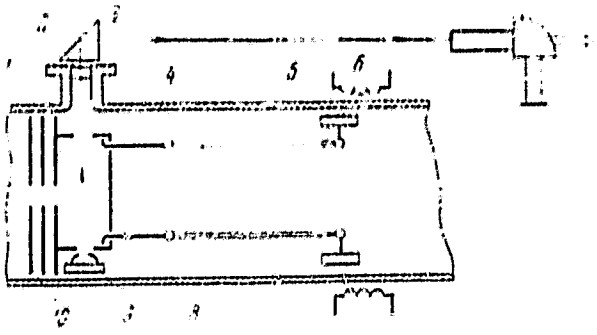

Fig. 3. Diagram of mass spectrometer ion source: 1. analyzer chamber; 2. inspection window; 3. rotating prism; 4. baffle; 5. permanent magnet; 6. electromagnet; 7. pyrometer; 8. ionization chamber; 9. vaporizer; 10. lens block.

cluded in the MI-1305 set were used. Both types of vaporizers were made of 0.03 mm thick tantalum, tungsten and molybdenum. These vaporizers, with a 0.3-0.5 mg load, permitted temperatures on the order of 2500 K to be obtained and studies to be conducted for at least six continuous hours without changing power packs. In addition to that, the ion source was supplemented with electromechanical shutters installed in the molecular beam path, to prevent dust coating of the pyrometry window; it permitted detection of the background spectrum level. The shutters are controlled remotely without breaking the vacuum. Remote control elements also are incorporated in the vaporizer power packs for convenience in operation. Finally, in order to reduce the energy of the ionizing electrons the outlet voltage divider is replaced in the ionizing voltage unit and remote and automatic components are incorporated to change the ionizing electron energy between 4.5 and 40 eV. This permits a significant /140 reduction in the time to obtain the vapor component ionization efficiency curves and an increase in accuracy of determination of the ion appearance potentials ($\lesssim$0.2 eV).

The changes noted permitted the conduct of studies of the composition of high-melting compound vapors in the 1300-2500 K temperature interval in the 1-400 amu mass number range, with a resolution of at least 250 and a sensitivity on the order of 10^{-10} atm, and determination of the temperature dependence of the vapor component ion current intensities (the product of the ion current intensity and temperature is proportional to the partial pressure). The latter, just as in the evaporation rate measurements, was used for calculation of the heats of reaction causing the appearance of different

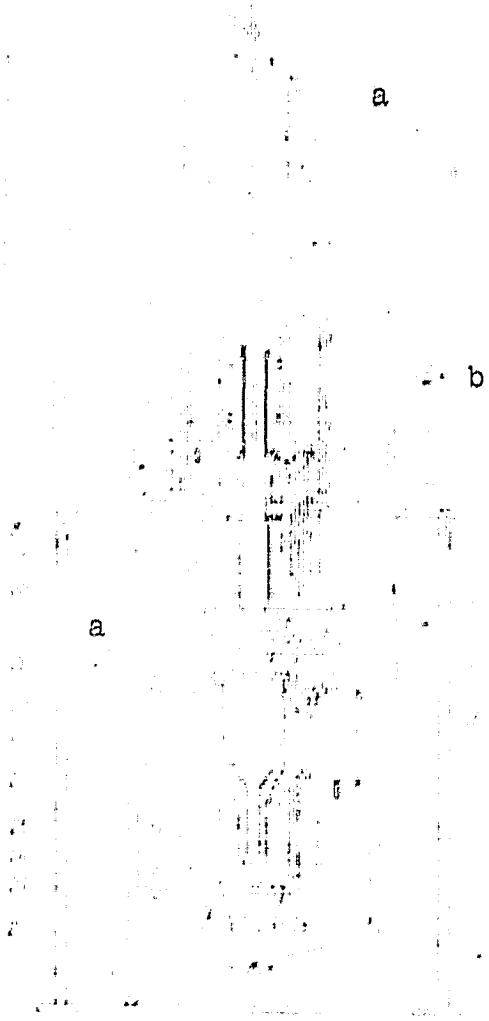

Fig. 4. Diagram of unit for measurement of heat content at temperatures of 1200-2500 K: 1. molybdenum rod; 2. tungsten lifting handle; 3, 30. vacuum shutoffs; 4. specimen; 5. furnace housing; 6. vacuum furnace; 7. furnace heater; 8, 9, 35, 37, 38. shields; 10, 17. shutters; 11. current buses; 12, 26, 31. coolers; 13. contact thermometer; 14, 25. heater; 15. mercury thermometer; 16. post; 18. copper block; 19. copper shields; 20. calorimeter shell; 21. thermostat shell; 22. lifting truck; 23. ebonite platform; 24. organic glass ring; 27. mixer; 28. funnel; 29. resistance thermometer; 32. contacts; 33. current leads; 34. molybdenum rod; 36. inspection window; 39. collar; 40. holder; 41. shields; 42. vacuum lock; 43. vacuum lock cover.

Key: a. To RVN-20 b. To VA-2-3

components in the vapor at the average test temperatures. So as to reduce the evaporation reaction characteristics determined at the average test temperatures in the equipment described to standard conditions, the thermodynamic functions of the members of the reactions must be known, particularly those of the high-melting compounds studied. Temperature vs. heat capacity or enthalpy is the foundation for calculation of the thermodynamic functions.

The experimental unit for measuring the heat content of materials by the mixing method in the 1200-2500 K temperature region (Fig. 4) consists of a high temperature furnace similar to the furnace of the automatic balance unit and the calorimetry system. The basic part of the calorimeter is a copper block with a weight of

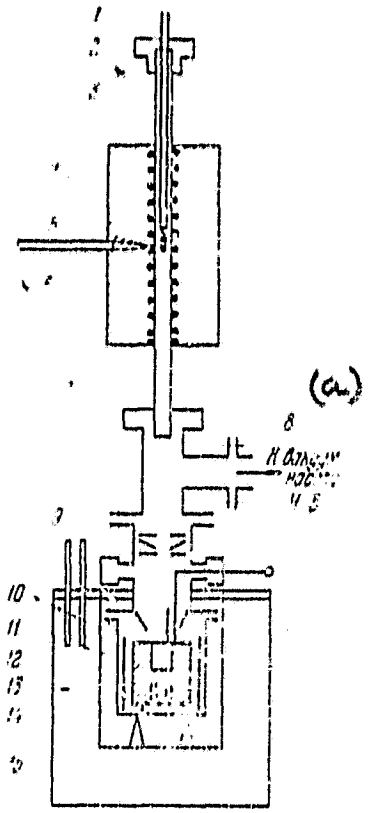

Fig. 5. Diagram of unit for study of enthalpy in 400-1300 K temperature interval: 1. chromel-alumel thermocouple; 2. top flange; 3. quartz tube; 4. furnace with nichrome heater; 5. test specimen; 6. platinum-platinorhodium thermocouple; 7. connecting flange; 8. side flange; 9. shutters; 10. calorimeter chamber; 11. shields; 12. calorimetry block; 13. heating unit; 14. organic glass ring; 15. thermostat.

Key: a. To N-5 vacuum pump

approximately 15 kg and built in nichrome heater and copper resistance thermometer with R=81.0842 ohm. The copper block, with chrome plated copper protective shields, is placed in a steel jacket, which is placed in a 30 ℓ capacity water thermostat. The calorimetry system is connected to the furnace by a cooled steel tube. The calorimetry system is protected from radiation by a water cooled shutoff (and during release of the specimen by a mica shutter). The lock type vacuum system of the calorimetry unit permits introduction of specimens to the operating zone of the furnace and their removal from the calorimetry unit without breaking the vacuum in the remaining portions of the unit. The working vacuum is $5 \cdot 10^{-6}$ mm Hg. /141

The resistance thermometer readings were recorded by means of a MOD-49 direct current bridge and a M-17 ballistic galvanometer. The systematic measurement errors in this unit are not over 1.2%, and the random error is not over 1.5%.

In the enthalpy measurement unit in the 400-1300 K interval (Fig. 5), a stainless steel tube with a 25 mm inside diameter was used instead of the vacuum chamber. The specimens were heated in a furnace with a nichrome heater. The tube was connected by means of vacuum seals to the top suspension flange and the vacuum chamber of the calorimetry block.

The top flange is used for hinge mounting of the transverse suspension of the specimen, which is tripped by burning a molybdenum filament, and for introduction of a chromel-alumel thermocouple into the quartz jacket for measurement of the specimen temperature. The vacuum chamber of the calorimetry unit is evacuated simultaneously with the quartz tube by a type N-5 pump (operating vacuum no poorer than $1 \cdot 10^{-4}$ mm Hg), and its lower portion is submerged in a TS-15 thermostat.

The calorimetry block of this unit also is copper and is equipped with a nichrome heater and copper thermometer (resistance R=72.322 ohm). Protection of the calorimetry block from the furnace radiation is provided by shutters which are opened by the dropping specimen. The resistance thermometer readings are recorded with a R-309 compensation bridge and M-17 ballistic galvanometer. The random measurement error in the unit is not over 1%.

The temperature vs. enthalpy permits determination of the temperature vs. heat capacity which, as is known, is the basis of calculation of the remaining thermodynamic functions of the material.

Thus, the instrument complex described permits determination of a number of thermophysical including thermodynamic characteristics of materials over a wide temperature interval, both under equilibrium and close to operating conditions. Studies of reference materials have shown that measurements made in the complex in question are in good agreement with the most reliable literature data.

The following have been studied by means of this complex: titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium and boron carbides; lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, ytterbium, titanium, zirconium, niobium, tantalum and iron borides; lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, ytterbium, hafnium, tantalum, chromium, molybdenum and tungsten sulfides; indium, scandium, lanthanum, samarium, titanium, zirconium, hafnium, niobium, boron, aluminum, germanium,

gallium, silicon and phosphorus nitrides; lanthanum, praseodymium, neodymium, samarium and europium selenides; chromium and lanthanum silicides; praseodymium and neodymium phosphides.

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